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Theoretical Study of Fireflies Light Emitter and its Analogues: Color Modulation

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► **To cite this version:**

Madjid Zemmouche, Cristina Garcia-Iriepa, Romain Berraud-Pache, Isabelle Navizet. Theoretical Study of Fireflies Light Emitter and its Analogues: Color Modulation. JTMS 2018 : Journées "Théorie, Modélisation et Simulation", May 2018, Paris, France. 14, pp.2117 - 2126, 2018. hal-01799623

HAL Id: hal-01799623

<https://hal.science/hal-01799623v1>

Submitted on 24 May 2018

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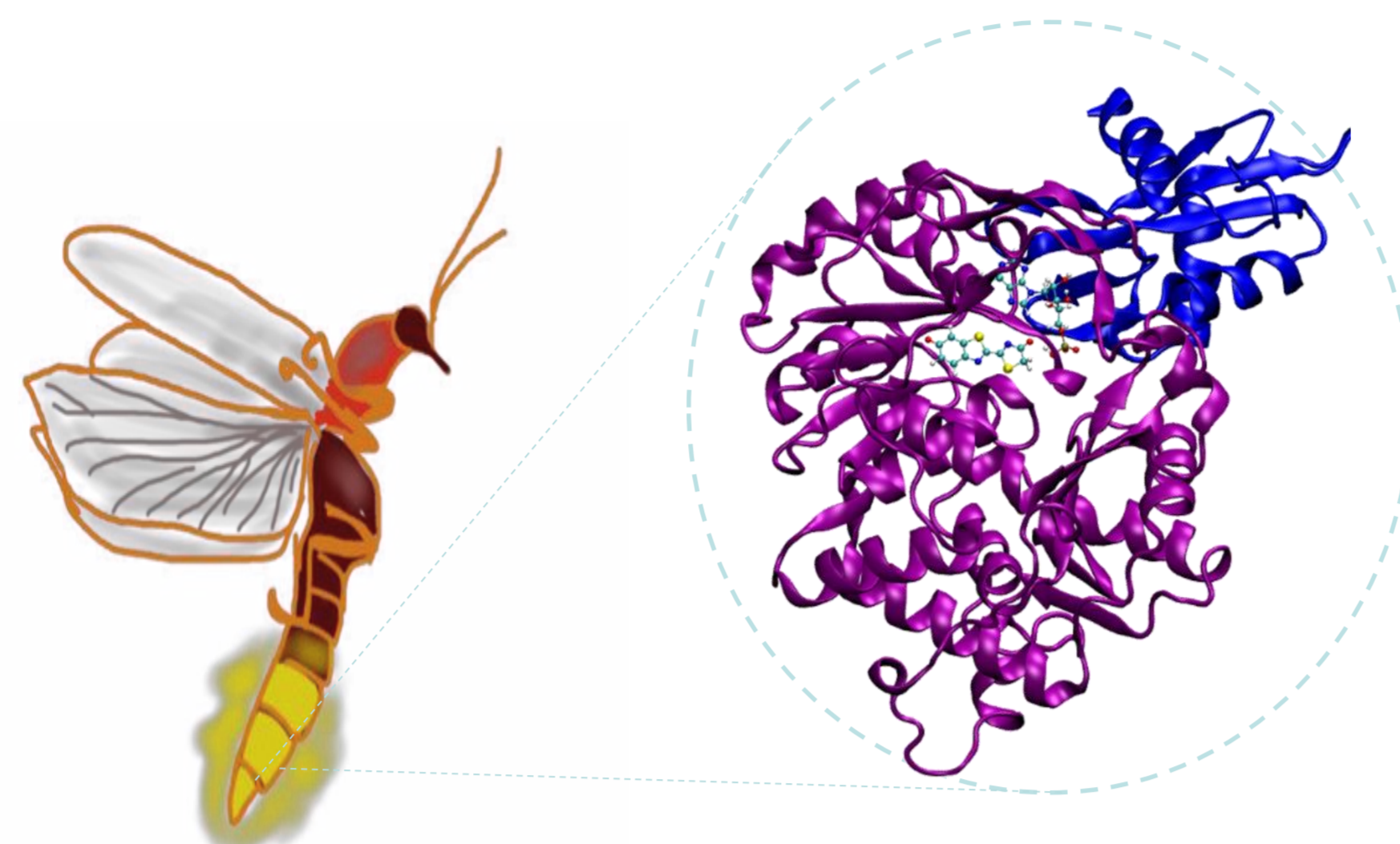
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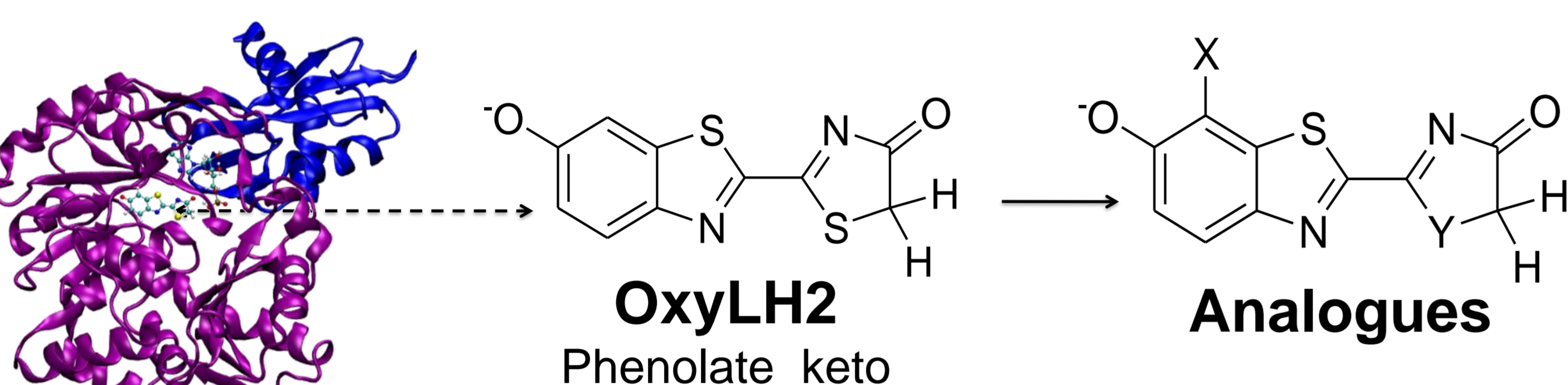
Firefly Bioluminescence

Bioluminescence is a spectacular phenomenon of light emission by some living organisms. It is caused by the oxidation of an organic molecule (luciferin) in the presence of dioxygen, which is catalyzed by the enzyme (luciferase). Light comes from the relaxation of the reaction product: oxyluciferin.^[1]



Experimenters have synthesized several analogues of oxyluciferin in order to understand the importance of the nature of the light emitter. They have modified the oxyluciferin compound by substituting atom by others (for example the sulfur by a carbon)^[2] or adding groups (like allyl group in the benzothiazole ring)^[3] on the luciferin compound and measured the bioluminescent emission spectra. We have performed theoretical study on the firefly oxyluciferin, light emitter and its synthesized analogues.^[2-3]

Molecules under study



Luciferase

| | | |
|--------------|--|---------------------|
| Carbo_oxylH2 | : X = H | Y = CH ₂ |
| OxyLH2 | : X = H | Y = S |
| Allyl_oxylH2 | : X = CH ₂ CH=CH ₂ | Y = S |

Methods

- G09, G09/Tinker
- In implicit water simulation
 - LR within TD-DFT using B3LYP functional and 6-311g(2d,p) as basis set
- In explicit water → MD Simulation 10 ns (Amber-ff99, oxyLH2 and carbo_oxylH2 parametrization)
 - 100 Snapshots
 - QM/MM excitation and emission energy calculation (TD-DFT/AMBER)
 - Absorption and emission spectra simulation

H-BOND

H-bonds pattern and number of H-bonds between H₂O and specific atoms during MD simulation of oxyLH2 and carbo_oxylH2

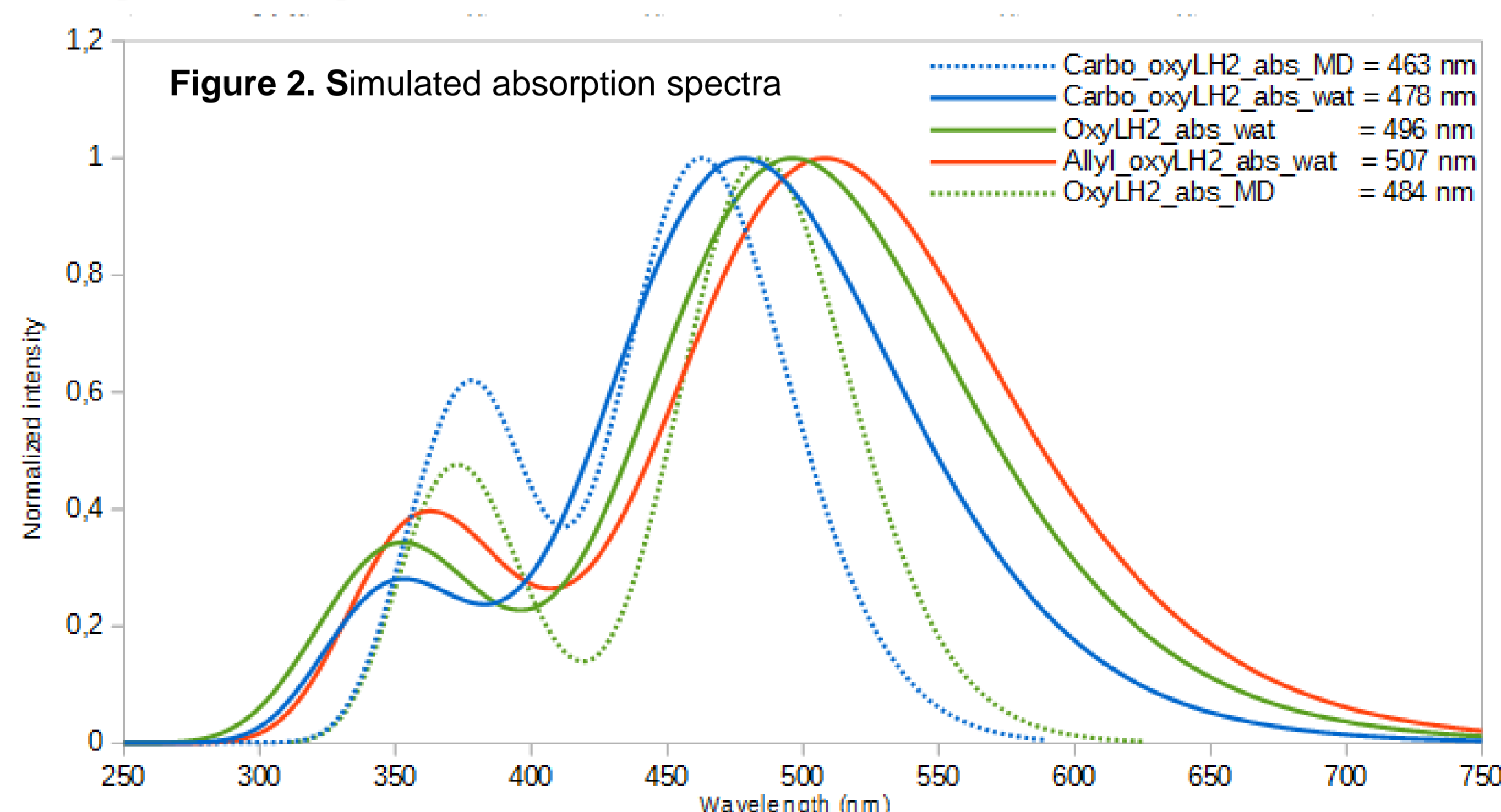
| Molecule | O _{ben} | O _{thia} | N _{thia} | N _{ben} |
|--------------|------------------|-------------------|-------------------|------------------|
| OxyLH2 | 3.2 | 2.2 | 0.2 | 0.4 |
| Carbo_oxylH2 | 3.3 | 2.4 | 0.2 | 0.2 |

H-bond interactions between the oxyLH2 (carbo_oxylH2) and the water molecules along the simulation time show nearly the same interactions.

Aims

- Determine the impact of the solvation modeling
- Determine the influence of modification in oxyluciferin on the color modulation in the absorption and emission
- Simulate the absorption and emission spectra in implicit and explicit water
- Compare the theoretical results with the available experimental^[2-3] ones.

Absorption Spectra Simulation



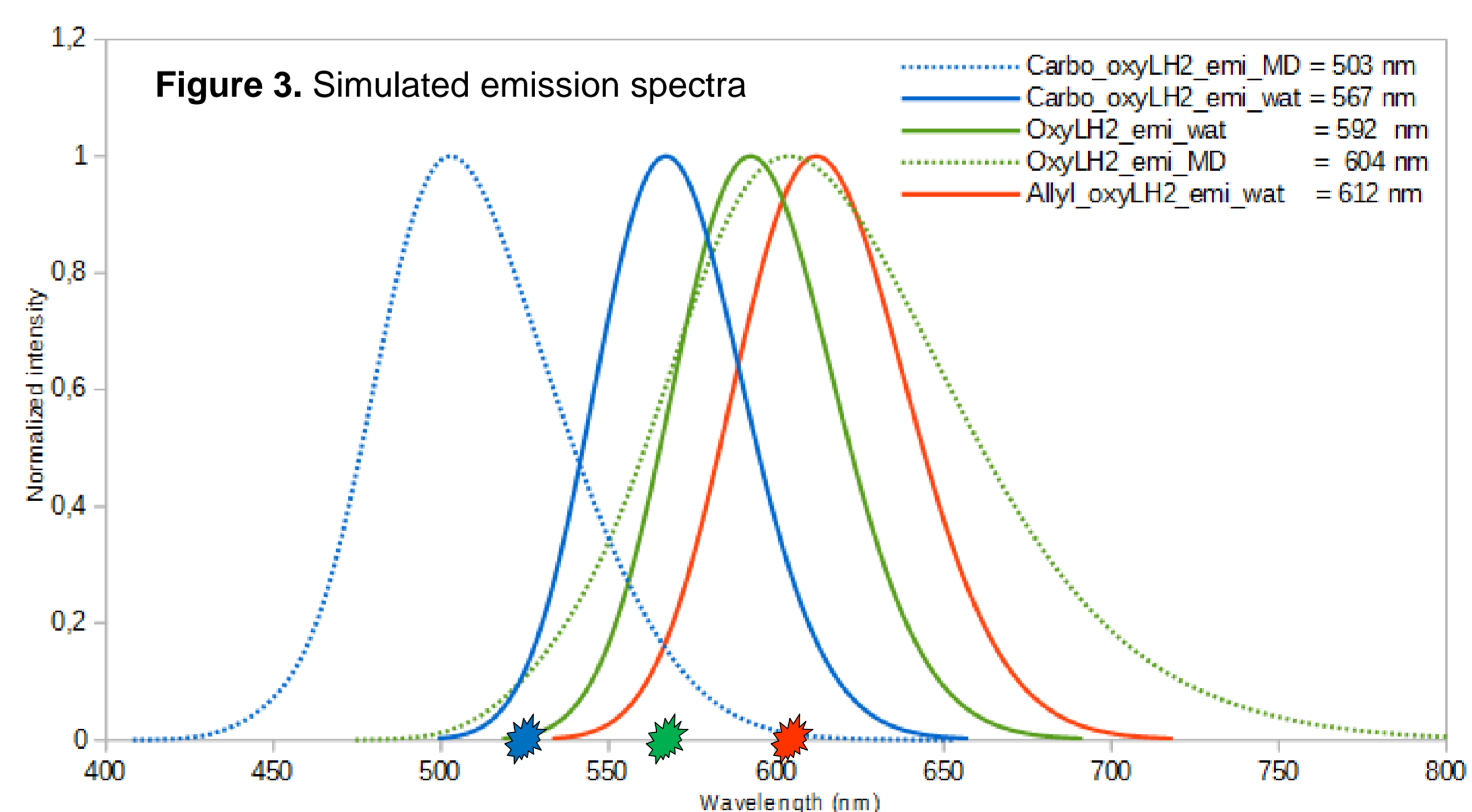
Modifications of the benzothiazole and thiazoline groups led to a change of absorption values, producing a red-shift in allyl_oxylH2 and blue-shift in carbo_oxylH2 for both absorption and emission.

Charge transfer in thiazolone ring and frontier orbitals involved in the emission S₀—S₁

| | Carbo_oxylH2 | OxyLH2 | Allyl_oxylH2 |
|------|--------------|--------|--------------|
| CT | -0.24e | -0.16e | -0.166e |
| LUMO | | | |
| HOMO | | | |

- Substitution at positions Y by a CH₂ group: blue-shift of the emission. It can be related to a bigger charge transfer.
- Adding an allyl group at position X: red-shift of the emission. No impact on the charge transfer.

Emission Spectra Simulation



- Experimental bioluminescence values (inside protein)
 - Carbo_oxylH2
 - OxyLH2
 - Allyl_oxylH2
- Explicit solvent or implicit solvent modeling give different wavelength.
- Results to be compared with experiment.